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## Description

### Age-resistant soft polyolefin wrapping foil

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This application is a 371 of PCT/EP2004/052208, filed September 16, 2004, which claims foreign priority benefit under 35 U.S.C. § 119 of the German Patent Application No. 103 48 483.3 filed October 14, 2003.

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The present invention relates to an age-resistant polyolefin wrapping foil, in particular a halogen-free, flame-retardant embodiment which is made from polypropylene copolymer and has been optionally provided with a pressure-sensitive adhesive coating, and which is used, for example, for wrapping ventilation lines in air-conditioning units, wires or cables, and which is suitable in particular for cable looms in vehicles or field coils for picture tubes. The wrapping foil serves for bundling, insulating, marking, sealing or protecting. The invention further embraces processes for producing the foil of the invention. The wrapping foil is notable for the use of specific aging inhibitor combinations such as antioxidants and metal deactivators in sufficient amount.

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Cable winding tapes and insulating tapes are normally composed of plasticized PVC film with a coating of pressure-sensitive adhesive on one side. There is an increased desire to eliminate disadvantages of these products. These disadvantages include plasticizer evaporation and high halogen content. Alternative polyolefin products have a limited aging stability. Moreover, they soften even at low temperatures. Excluded from this are polypropylene and its copolymers; unfortunately, their aging stability is particularly poor as compared with the readily melting polyolefins such as PE or EVA. If it is desired to make appropriate additions in order to render such a winding tape flame-retardant, there is a further decrease in aging stability.

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The plasticizers in conventional insulating tapes and cable winding tapes gradually evaporate, leading to a health hazard; the commonly used DOP, in particular, is objectionable. Moreover, the vapors deposit on the glass in motor vehicles, impairing visibility (and hence, to a considerable extent, driving safety), this being known to the skilled worker as fogging (DIN 75201). In the event of even greater vaporization as a result of higher temperatures, in the engine compartment of vehicles, for example, or in electrical equipment in the case of insulating tapes, the wrapping foil is embrittled by the accompanying loss of plasticizer.

Plasticizers impair the fire performance of unadditized PVC, something which is compensated in part by adding antimony compounds, which are highly objectionable from the standpoint of toxicity, or by using chlorine- or phosphorus-containing plasticizers.

Against the background of the debate concerning the incineration of plastic wastes, such as shredder waste from vehicle recycling, for example, there exists a trend toward reducing the halogen content and hence the formation of dioxins. In the case of cable insulation, therefore, the wall thicknesses are being reduced, and the thicknesses of the PVC film are being reduced in the case of the tapes used for wrapping. The standard thickness of the PVC films for winding tapes is 85 to 200  $\mu\text{m}$ . Below 85  $\mu\text{m}$ , considerable problems arise in the calendering operation, with the consequence that virtually no such products with reduced PVC content are available.

The customary winding tapes comprise stabilizers based on toxic heavy metals, usually lead, more rarely cadmium or barium.

State of the art for the bandaging of sets of leads are wrapping foils with and without an adhesive coating, said films being composed of a PVC carrier material which has been made flexible through incorporation of considerable amounts (30 to 40% by weight) of plasticizer. The carrier material is coated usually on one side with a self-adhesive mass based on SBR rubber. Considerable deficiencies of these adhesive PVC winding tapes are their low aging stability, the migration and evaporation of plasticizer, their high halogen content, and a high smoke gas density in the event of fire. JP 10 001 583 A1, JP 05 250 947 A1, JP 2000 198 895 A1 and JP 2000 200 515 A1 describe typical plasticized PVC adhesive tapes. In order to obtain higher flame retardancy in the

plasticized PVC materials it is usual, as described for example in JP 10 001 583 A1, to use the highly toxic compound antimony oxide.

There are attempts to use wovens or nonwovens instead of plasticized PVC film; however the products resulting from such attempts are but little used in practice, since they are relatively expensive and differ sharply from the habitual products in terms of handling (for example, hand tearability, elastic resilience) and under service conditions (for example, resistance to service fluids, electrical properties), with – as set out below – particular importance being attributed to the thickness.

DE 200 22 272 U1, EP 1 123 958 A1 and WO 99/61541 A1 describe adhesive winding tapes comprising a clothlike (woven) or weblike (nonwoven) carrier material. These materials are distinguished by a very high tensile strength. A consequence of this, however, is the disadvantage that, when being processed, these adhesive tapes cannot be torn off by hand without the assistance of scissors or knives.

Stretchability and flexibility are two of the major requirements imposed on adhesive winding tapes, in order to allow the production of crease-free, flexible cable harnesses. Moreover, these materials do not meet the relevant fire protection standards such as FMVSS 302. Improved fire properties can be realized only with the use of halogenated flame retardants or polymers as described in US 4,992,331 A1.

In modern-day vehicle construction, on the one hand the cable harnesses are becoming increasingly rigid and thicker as a result of the multiplicity of electrical consumer units and the increased transfer of information within vehicles, while on the other hand the space for their installation is becoming ever more greatly restricted, and, consequently, assembly (guidethrough when laying cables within the vehicle body) is becoming more problematic. As a result, a thin film tape is advantageous. Moreover, for efficient and cost-effective cable harness production, cable winding tapes are expected to have easy and quick processing qualities.

Winding tapes based on plasticized PVC films are used in automobiles for bandaging electrical leads to form cable harnesses. Although initially the primary technical purpose was to improve the electrical insulation when using these winding tapes, which were originally developed as insulating tapes, cable harness tapes of this kind are now required to fulfill further functions, such as the bundling and permanent fixing of a multiplicity of individual cables to form a stable cable strand, and the protection of the

individual cables and the entire cable strand against mechanical, thermal, and chemical damage.

5 DE 199 10 730 A1 describes a laminate carrier which is composed of velour or foam and a nonwoven, and which is adhesively bonded by means of a double-sided adhesive tape or using a hotmelt adhesive.

10 EP 0 886 357 A2 describes a triple-ply protective sheath comprising a spunbonded web, a PET knit, and a strip of foam or felt, which are laminated together, the protective sheath additionally being provided, at least in part, and very complicatedly, with adhesive strips and touch-and-close fastener systems.

15 EP 1 000 992 A1 describes a holed cotton nonwoven which has a polyethylene coating 10 to 45  $\mu\text{m}$  thick and also has an additional release coating.

DE-U 94 01 037 describes an adhesive tape having a tapelike textile carrier composed of a stitchbonded web formed in turn from a multiplicity of sewn-in stitches which run parallel to one another. The web proposed therein is said to have a thickness of 150 to 400  $\mu\text{m}$  for a basis weight of 50 to 200  $\text{g}/\text{m}^2$ .

20 DE 44 42 092 C1 describes an adhesive tape based on stitchbonded web which is coated on the reverse of the carrier. DE 44 42 093 C1 is based on the use of a web as a carrier for an adhesive tape, said web being a cross-laid fiber web which is reinforced by the formation of loops from the fibers of the web, i.e., a web known to the skilled worker under the name Malifleece. DE 44 42 507 C1 discloses an adhesive tape for cable bandaging, but bases it on what are known as Kunit or Multiknit webs. All three documents use webs having a basis weight of approximately 100  $\text{g}/\text{m}^2$ , as can be inferred from the examples.

30 DE 195 23 494 C1 discloses the use of an adhesive tape with a nonwoven material carrier having a thickness of 400 to 600  $\mu\text{m}$  for bandaging cable harnesses, said tape being coated on one side with an adhesive.

35 DE 199 23 399 A1 discloses an adhesive tape having a tapelike carrier made of nonwoven material, which is coated on at least one side with an adhesive, the nonwoven web having a thickness of 100  $\mu\text{m}$  to 3000  $\mu\text{m}$ , especially 500 to 1000  $\mu\text{m}$ .

Webs with this kind of thickness make the cable harnesses even thicker and more inflexible than conventional PVC tapes, albeit with a positive effect on soundproofing, which is of advantage only in certain areas of cable harnesses. Webs, however, lack stretchability and exhibit virtually no resilience. This is of importance on account of the fact that thin branches of cable harnesses must be wound with sufficient tautness that, when installed, they do not hang down loosely, and such that they can easily be positioned before the plugs are clipped on and attached.

A further disadvantage of textile adhesive tapes is the low breakdown voltage of about 1 kV, since only the adhesive layer is insulating. Film-based tapes, in contrast, are situated at more than 5 kV; they have good voltage resistance.

Wrapping foils and cable insulation comprising thermoplastic polyester are being used on a trial basis for producing cable harnesses. They have considerable deficiencies in terms of their flexibility, processing qualities, aging stability, and compatibility with the cable materials. The gravest disadvantage of polyester, however, is its considerable sensitivity to hydrolysis, which rules out use in automobiles on safety grounds.

DE 100 02 180 A1, JP 10 149 725 A1, JP 09 208 906 A1 and JP 05 017 727 A1 describe the use of halogen-free thermoplastic polyester carrier films. JP 07 150 126 A1 describes a flame-retardant wrapping foil comprising a polyester carrier film which comprises a brominated flame retardant.

Also described in the patent literature are winding tapes comprising polyolefins. These, however, are readily flammable or comprise halogenated flame retardants. Furthermore, the materials prepared from ethylene copolymers have too low a softening point (in general they melt even during an attempt to test them for stability to thermal aging), and in the case of the use of polypropylene polymers the material is too inflexible.

WO 00/71634 A1 describes an adhesive winding tape whose film is composed of an ethylene copolymer base material. The carrier film comprises the halogenated flame retardant decabromodiphenyl oxide. The film softens below a temperature of 95°C, but the normal service temperature is often above 100°C or even briefly above 130°C, which is not unusual in the case of use in the engine compartment. Antioxidants are not mentioned.

WO 97/05206 A1 describes a halogen-free adhesive winding tape whose carrier film is composed of a polymer blend of low-density polyethylene with an ethylene/vinyl acetate or ethylene/acrylate copolymer. The flame retardant used is 20 to 50% by weight of aluminum hydroxide or ammonium polyphosphate. A considerable disadvantage of the carrier film is, again, the low softening temperature. To counter this the use of silane crosslinking is described. This crosslinking method, however, leads only to material with very nonuniform crosslinking, so that in practice it is not possible to realize a stable production operation or uniform product quality. Mention is made solely of the use of Irganox 1010 as primary antioxidant.

Similar problems of deficient heat distortion resistance occur with the electrical adhesive tapes described in WO 99/35202 A1 and US 5,498,476 A1. The carrier film material described is a blend of EPDM and EVA in combination with ethylenediamine phosphate as flame retardant. Like ammonium polyphosphate, this flame retardant is highly sensitive to hydrolysis. In combination with EVA, moreover, there is an embrittlement on aging. Application to standard cables of polyolefin and aluminum hydroxide or magnesium hydroxide results in poor compatibility. Furthermore, the fire performance of such cable harnesses is poor, since these metal hydroxides act antagonistically with phosphorus compounds, as set out below. The insulating tapes described are too thick and too rigid for cable harness winding tapes. A possible use of antioxidants is mentioned in WO 99/35202 A1, without any quantities or types being specified. US 5,498,476 A1 cites merely primary antioxidants, at 0.15 phr.

Attempts to resolve the dilemma of excessively low softening temperature, flexibility and freedom from halogen are described by the patents below.

EP 0 953 599 A1 claims a polymer blend of LLDPE and EVA for applications as cable insulation and as film material. The flame retardant described comprises a combination of magnesium hydroxide of specific surface area and red phosphorus; however, softening at a relatively low temperature is accepted. The only antioxidant mentioned is the primary antioxidant Irganox 1010, at 0.2 phr.

A very similar combination is described in EP 1 097 976 A1. In this case, though, for the purpose of improving the heat distortion resistance, the LLDPE is replaced by a PP polymer, which has a higher softening temperature. A disadvantage, however, is the



resultant low flexibility. For blending with EVA or EEA it is maintained that the film has sufficient flexibility. From the literature, however, the skilled worker is aware that these polymers are blended with polypropylene in order to improve flame retardancy. The products described have a film thickness of 0.2 mm: this thickness alone rules out flexibility in the case of filled polyolefin films, since flexibility is dependent on the thickness to the 3rd power. With the extremely low melt indices of the polyolefins used, as the skilled worker is aware, the described process of extrusion is virtually impossible to carry out on a production installation, and certainly not for a thin film in conformity to the art, and certainly not in the case of use in combination with the high amounts of filler that are described. A possible use of antioxidants is mentioned, without any quantities or types being specified. The attempted solution builds on the known synergistic flame retardancy effect of red phosphorus with magnesium hydroxide. The use of elemental phosphorus, however, harbors considerable disadvantages and risks. In the course of processing, foul-smelling and highly toxic phosphine is released. A further disadvantage arises from the development of very dense white smoke in the event of fire. Moreover, only brown to black products can be produced, whereas for color marking wrapping foils are used in a broad color range.

WO 03/070848 A1 describes a reactive polypropylene and 40 phr of magnesium hydroxide. This added amount is not enough for any substantial improvement in fire performance. The possible use of aging inhibitor, though mentioned, is not described in any detail (and not in inventive or comparative example). The use of carbon black or spherical magnesium hydroxide has not been described.

DE 203 06 801 U describes a polyurethane winding tape; such a product is much too expensive for the usual applications described above. There are no references to the use of aging inhibitors or magnesium hydroxide.

The cited patents of the prior art, despite the specified disadvantages, do not set out films which also achieve the further requirements such as hand tearability, thermal stability, compatibility with polyolefin cable insulation, or adequate unwind force. Furthermore, the processing qualities in film production operations, the high fogging number, and the breakdown voltage resistance remain questionable.

The object therefore remains to discover a solution for an aging-stable wrapping foil which combines the advantages of age resistance, flame retardancy, abrasion resistance,

voltage resistance and mechanical properties (such as elasticity, flexibility, and hand tearability) of PVC winding tapes with the freedom from halogen of textile winding tapes and, in particular, exhibits superior thermal aging resistance, in tandem with the need to ensure that the film can be produced industrially and that it has a high breakdown voltage resistance and a high fogging number in the case of certain applications.

It is an object of the invention, furthermore, to provide soft, aging-stable wrapping foils, in particular in halogen-free, flame-retardant embodiment, which allow particularly reliable and rapid wrapping, particularly of wires and cables, for the purpose of marking, protecting, insulating, sealing or bundling, where the disadvantages of the prior art do not occur, or at least not to the same extent.

It is a further object of the invention to achieve the requisite wrapping foil flexibility despite considerable amounts of flame retardants. The problem is disproportionately more difficult to solve in the case of a polyolefin winding tape than in the case of PVC, since in the case of PVC the need for flame retardant is low or absent and the flexibility is readily achievable by means of conventional plasticizers.

In concert with the increasingly complex electronics and the increasing number of electrical consumer units in automobiles, the sets of leads, too, are becoming ever more complex. With increasing cable harness cross sections, the inductive heating is becoming greater and greater, while the removal of heat is decreasing. As a result there are increases in the thermal stability requirements of the materials used. The PVC materials used as standard for adhesive winding tapes are reaching their limits here. A further object is therefore to find polyolefins with additive combinations which not only match but indeed exceed the thermal stability of PVC.

This object is achieved by means of a wrapping foil as specified in the main claim. The dependent claims relate to advantageous developments of the wrapping foil of the invention and to its use in a soft, age-resistant adhesive tape, to further applications thereof, and to processes for producing the wrapping foil.

The invention accordingly provides a soft, age-resistant, polyolefin wrapping foil, in particular a halogen-free, flame-retardant embodiment, comprising polypropylene copolymer and provided preferably with a pressure-sensitive adhesive coating.

The amounts below in phr denote parts by weight of the component in question per 100 parts by weight of all polymer components of the foil. In the case of a wrapping foil with



coating (with adhesive, for example) only the parts by weight of all polymer components of the polyolefin-containing layer are taken into account.

In order to achieve effective aging stability and compatibility the use of the correct aging inhibitors is assigned a particular role. In this context it is also necessary to take account of the total amount of aging inhibitor, since previously in the production of such winding tapes aging inhibitors were used not at all or only at below 0.3 phr (x phr denotes x parts per 100 parts of polymer or polymer blend), as is also usually the case for the production of other films. In particular, no secondary antioxidants were used either.

The winding tapes of the invention contain at least 4 phr of a primary antioxidant or at least 0.3 phr of a combination of primary and secondary antioxidants, it being possible for the primary and secondary antioxidant functions to be present in different molecules or to be united in one molecule. The amounts recited do not include optional stabilizers such as metal deactivators or light stabilizers.

The amount of secondary antioxidant is preferably at least 0.5 phr, in particular at least 1 phr.

Stabilizers for PVC products cannot be transferred to polyolefins. Secondary antioxidants break down peroxides and are therefore used as part of aging inhibitor packages in the case of diene elastomers. Surprisingly it has been found that a combination of primary antioxidants (for example, sterically hindered phenols or C-radical scavengers such as CAS 181314-48-7) and secondary antioxidants (for example, sulfur compounds, phosphites or sterically hindered amines), it also being possible for both functions to be united in one molecule, achieves the stated object in the case of diene-free polyolefins such as polypropylene as well. Particularly preferred is the combination of primary antioxidant, preferably sterically hindered phenols having a molecular weight of more than 500 g/mol (preferably > 700 g/mol), with a phosphitic secondary antioxidant (preferably having a molecular weight > 600 g/mol).

Phosphites or a combination of primary and two or more secondary aging inhibitors have not been used to date in wrapping foils comprising polyolefins such as polypropylene polymers.

The combination of a low-volatility primary phenolic antioxidant and in each case a secondary antioxidant from the class of the sulfur compounds (preferably having a molecular weight of more than 400 g/mol, in particular > 500 g/mol) and from the class of the phosphites is particular suitable, it not being necessary for the phenolic, the sulfur-

containing, and the phosphitic functions to be present in three different molecules; instead, more than one function may also be united in one molecule.

Examples:

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- Phenolic function:

CAS 6683-19-8, 2082-79-3, 1709-70-2, 36443-68-2, 1709-70-2, 34137-09-2, 27676-62-6, 40601-76-1, 31851-03-3, 991-84-4

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- Sulfur-containing function:

CAS 693-36-7, 123-28-4, 16545-54-3, 2500-88-1, 16545-34-3, 29598-76-3

- Phosphitic function:

15 CAS 31570-04-4, 26741-53-7, 80693-00-1, 140221-14-3, 119345-01-6, 3806-34-6, 80410-33-9, 14650-60-8, 161717-32-4

- Phenolic and sulfur-containing function:

CAS 41484-35-9, 90-66-4, 110553-27-0, 96-96-5, 41484

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- Phenolic and aminic function:

CAS 991-84-4, 633843-89-0

- Aminic function:

CAS 52829-07-9, 411556-26-7, 129757-67-1, 71878-19-8, 65447-77-0

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The combination of CAS 6683-19-8 (for example, Irganox 1010) with thiopropionic ester CAS 693-36-7 (Irganox PS 802) or 123-28-4 (Irganox PS 800) with CAS 31570-04-4 (Irgafos 168) is particularly preferred. Preference is given further to a combination in which the fraction of secondary antioxidant exceeds that of the primary antioxidant. In addition it is possible to add metal deactivators in order to complex traces of heavy metal, which may catalytically accelerate aging. Examples are CAS 32687-78-8, 70331-94-1, 6629-10-3, ethylenediaminetetraacetic acid, N,N'-disalicylidene-1,2-diaminopropane, 3-(N-salicylol)amino-1,2,4-triazole (Palmarole ADK STAB CDA-1), N,N'-bis[3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionyl]hydrazide (Palmarole MDA.P.10) or 2,2'-oxamido-bis[ethyl 3-(tert-butyl-4-hydroxyphenyl)propionate] (Palmarole MDA.P.11).

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When more than about 0.5 phr of a thiopropionic ester is used it is possible for said ester to migrate to the surface, which in the case of black foils is visible in a particularly unattractive way. The problem can be solved, surprisingly, by combining different thiopropionic esters such that for each thiopropionic ester the solubility limit is not exceeded. Preference is therefore given to a combination of two or more thiopropionic esters. This is most simply accomplished by varying the alkyl chains.

The selection of the stated aging inhibitors is particularly important for the wrapping foil of the invention, since with phenolic antioxidants, alone or even in combination with sulfur-containing costabilizers, it is not generally possible to obtain products which conform to the art. In the case of calender processing, where on the rolls a relatively long-lasting ingress of atmospheric oxygen is unavoidable, the concomitant use of phosphite stabilizers proves virtually inevitable for sufficient thermal aging stability on the part of the product. Even in the case of extrusion processing the addition of phosphites is still manifested positively in the aging test on the product.

For the phosphite stabilizer an amount of at least 0.1 phr, preferably at least 0.3 phr, is preferred. Particularly when using natural magnesium hydroxides such as brucite it is possible, as a result of migratable metal impurities such as iron, manganese, chromium or copper, for aging problems to arise, which can be avoided only through abovementioned knowledge of the correct combination and amount of aging inhibitors. As remarked above, ground brucite has a number of technical advantages over precipitated magnesium hydroxide, so that the combination with antioxidants as described is particularly sensible. For applications involving a high temperature load (for example, for use as cable wrapping foil in the engine compartment of motor vehicles or as an insulating winding on magnet coils in TV or PC screens) an embodiment is preferred which besides the antioxidants also includes a metal deactivator.

The thickness of the film of the invention is in the range from 30 to 180  $\mu\text{m}$ , preferably 50 to 150  $\mu\text{m}$ , in particular 55 to 100  $\mu\text{m}$ . The surface may be textured or smooth. Preferably the surface is made slightly matt. This can be achieved through the use of a filler having a sufficiently high particle size or by means of a roller (for example, embossing roller on the calender or matted chill roll or embossing roller during extrusion).

In a preferred version the film is provided on one or both sides with a pressure-sensitively adhesive layer, in order to simplify application, so that there is no need to fasten the wrapping foil at the end of the winding operation.

- 5 The wrapping foil of the invention is substantially free from volatile plasticizers such as DOP or TOTM, for example, and therefore has excellent fire performance and low emissions (plasticizer evaporation, fogging).

10 Unforeseeably and surprisingly for the skilled worker a wrapping foil of this kind can be produced from polyolefin and suitable aging inhibitor combinations and in particular with flame-retardant fillers such as magnesium hydroxide. Remarkably, in addition, the thermal aging stability, in comparison to PVC as a high-performance material, is not poorer but instead is comparable or even better.

- 15 The wrapping foil of the invention has advantageously in machine direction a force at 1% elongation of 0.6 to 4 N/cm, preferably of 1 to 3 N/cm, and at 100% elongation a force of 2 to 20 N/cm, preferably of 3 to 10 N/cm.

20 In particular the force at 1% elongation is greater than or equal to 1 N/cm and the force at 100% elongation is less than or equal to 15 N/cm. The 1% force is a measure of the rigidity of the film, and the 100% force is a measure of the conformability when it is wound with sharp deformation as a result of high winding tension. The 100% force must also not be too low, since otherwise the tensile strength is inadequate.

- 25 In order to achieve these force values the wrapping foil preferably comprises at least one polyolefin having a flexural modulus of less than 900 MPa, preferably 500 MPa or less, and in particular of 80 MPa or less. The polyolefin may be a soft ethylene homopolymer or ethylene or propylene copolymer. A propylene copolymer is preferred.

- 30 The preferred melt index for calender processing is below 5 g/10 min, preferably below 1 g/10 min, and in particular below 0.7 g/10 min. For extrusion processing the preferred melt index is between 1 and 20 g/10 min, in particular between 5 and 15 g/10 min.

35 The crystallite melting point of the polyolefin is advantageously between 120°C and 166°C, preferably below 148°C, more preferably below 145°C.

The crystalline region of the copolymer is preferably a polypropylene having a random structure, in particular with an ethylene content of 6 to 10 mol%. A polypropylene random copolymer modified (with ethylene, for example) has a crystallite melting point, depending on the block length of the polypropylene and the comonomer content of the amorphous phase, of between 120°C and 145°C (this is the range for commercial products). Depending on molecular weight and tacticity, a polypropylene homopolymer is situated at between 163°C to 166°C. If the homopolymer has a low molecular weight and has been modified with EP rubber (for example grafting, reactor blend), then the reduction in melting point leads to a crystallite melting point in the range from about 148°C to 163°C. For the polypropylene copolymer of the invention, therefore, the preferred crystallite melting point is below 145°C and is best achieved with a comonomer-modified polypropylene having random structure in the crystalline phase and a copolymeric amorphous phase.

In such copolymers there is a relationship between the comonomer content of both the crystalline phase and the amorphous phase, the flexural modulus, and the 1% tension value of the wrapping foil produced therefrom. A high comonomer content in the amorphous phase allows a particularly low 1% force value. Surprisingly, the presence of comonomer in the hard crystalline phase as well has a positive effect on the flexibility of the filled foil.

The crystallite melting point ought, however, not to be below 120°C, as is the case for EPM and EPDM, since in the event of applications on ventilation pipes, screen coils or vehicle cables there is a risk of melting. Wrapping foils comprising ethylene-propylene copolymers from the classes of the EPM and EPDM are therefore not in accordance with the invention, although this does not rule out using such polymers to fine-tune the mechanical properties alongside the polypropylene copolymer of the invention.

There are no restrictions imposed on the monomer or monomers of the polyolefin, although preference is given to using  $\alpha$ -olefins such as ethylene, propylene, 1-butylene, isobutylene, 4-methyl-1-pentene, hexene or octene. Copolymers having three or more comonomers are included for the purposes of this invention. Particularly preferred monomers for the polypropylene copolymer are propylene and ethylene. The polymer may additionally have been modified by grafting, for example with maleic anhydride or acrylate monomers, for the purpose of improving the processing properties or mechanical properties, for example. By polypropylene copolymer is meant not only copolymers in the

strict sense of polymer physics, such as block copolymers, for example, but also commercially customary thermoplastic PP elastomers with a wide variety of structures or properties. Materials of this kind may be prepared, for example, from PP homopolymers or random copolymers as a precursor by further reaction with ethylene and propylene in the gas phase in the same reactor or in subsequent reactors. When random copolymer starting material is used the monomer distribution of ethylene and propylene in the EP rubber phase which forms is more uniform, leading to improved mechanical properties. This is another reason why a polymer with a crystalline random copolymer phase is preferred for the wrapping foil of the invention. For the preparation it is possible to employ conventional processes, examples including the gas-phase process, Cataloy process, Spheripol process, Novolen process, and Hypol process, which are described in Ullmann's Encyclopedia of Industrial Chemistry, 6th ed., Wiley-VCH 2002.

Suitable blend components are, for example, soft ethylene copolymers such as LDPE, LLDPE, metallocene-PE, EPM or EPDM with a density of 0.86 to 0.92 g/cm<sup>3</sup>, preferably from 0.86 to 0.88 g/cm<sup>3</sup>. Soft hydrogenated random or block copolymers of ethylene or (unsubstituted or substituted) styrene and butadiene or isoprene are also suitable for bringing the flexibility, the force at 1% elongation, and, in particular, the shape of the force/elongation curve of the wrapping foil into the optimum range. If in addition to the polypropylene copolymer of the invention a further ethylene or propylene copolymer is used it preferably has a specified melt index in the range of  $\pm 50\%$  of the melt index of the polypropylene copolymer. This is without taking into account the fact that the melt index of ethylene copolymers is generally specified for 190°C and not, as in the case of polypropylene, for 230°C.

By using ethylene copolymers with carbonyl-containing monomers such as ethylene acrylate (for example EMA, EBA, EEA, EAA) or ethylene-vinyl acetate it is possible, as the skilled worker is aware, to improve the fire performance of PP polymers. This also applies to the wrapping foil of the invention with a polymer having the properties specifically required here. Furthermore, it is found and claimed that polyethylene-vinyl alcohol and olefin-free nitrogen- or oxygen-containing polymers are also suitable as synergists, in the form for example of polyvinyl alcohol, polyamides and polyesters having a sufficiently low softening point (fitting in with the processing temperature of polypropylene), polyvinyl acetate, polyvinyl butyral, vinyl acetate-vinyl alcohol copolymer, and poly(meth)acrylates. These highly polar materials are considered by the skilled worker to be incompatible with polypropylene, since the solubility parameter is at least



19 J<sup>1/2</sup>/cm<sup>3/2</sup>. Surprisingly, in the case of the inventive blending of specific copolymer and flame-retardant filler, this proves to be no problem. Preference is given to polyvinyl acetate and poly(meth)acrylates, which may also have been crosslinked. They may also have a core-shell structure: for example, a core of polyacrylates of alcohols having 2 to 8 carbon atoms and a shell of polymethyl methacrylate. In particular, acrylate impact modifiers, which are prepared for the modification of PVC, prove particularly suitable, since even in small amounts they produce a marked improvement in the fire performance, while not substantially impairing the flexibility of the wrapping foil and, in spite of their polarity, not increasing the sticking of the melt on calender rolls or chill rolls.

A further possibility lies in the use of polyolefins in which the oxygen is introduced by grafting (for example, with maleic anhydride or with a (meth)acrylate monomer). In one preferred embodiment the fraction of oxygen, based on the total weight of all polymers, is between 0.5 and 5 phr (corresponding also to % by weight), in particular 0.8 to 3 phr. If besides the polypropylene copolymer of the invention a thermoplastic oxygen- or nitrogen-containing polymer is used, it preferably has a specified melt index in the range of  $\pm 50\%$  of the melt index of the polypropylene copolymer.

One specific embodiment is a wrapping foil having at least one coextrusion layer comprising a nitrogen- or oxygen-containing polymer, which may have been provided with the flame retardants and aging inhibitors or carbon blacks disclosed herein, as well as a layer of polypropylene copolymer.

Suitable flame retardants are essentially only halogen-free materials; that is, for example, fillers such as polyphosphates, carbonates and hydroxides of aluminum and/or of magnesium, borates, stannates, and nitrogen-based organic flame retardants.

Preference is given to

- a) combinations of phosphates (for example, ammonium polyphosphate or ethylenediamine polyphosphate) and nitrogen compounds, and especially
- b) hydroxides of magnesium.

Polyphosphates and nitrogen compounds are suitable but in part are sensitive to water. This may lead to corrosion or to impairments in the electrical properties such as the breakdown voltage. Water inflow is not significant for a wrapping foil in the passenger compartment. In the engine compartment, however, the wrapping foil may become hot and wet. Examples of nitrogen-containing flame retardants are dicyandiamide, melamine

cyanurate and sterically hindered amines such as, for example, the class of the HA(L)S. Red phosphorus can be used but preferably is not (in other words, the amount is zero or not flame-effective), since its processing is hazardous (self-ignition of liberated phosphine during incorporation into the polymer by mixing; even in the case of coated phosphorus the amount of phosphine produced may still be enough to pose a health hazard to operatives). Moreover, when red phosphorus is used, it is not possible to produce colored products, but only black and brown products.

A preferred filler as flame retardant is magnesium hydroxide, especially in combination with nitrogen-containing flame retardants. Examples of nitrogen-containing flame retardants are melamine, ammeline, melam, and melamine cyanurate. As is known from the literature, red phosphorus likewise has a synergistic action when magnesium hydroxide is used. For the reasons set out above, however, it is preferably not used. Organic and inorganic phosphorus compounds in the form of the known flame retardants such as those, for example, based on triaryl phosphate, or polyphosphate salts, act antagonistically. In the preferred embodiments, therefore, bonded phosphorus is not used, unless it is in the form of phosphites having an inhibitory effect on aging. These phosphites should not exceed the chemically bonded phosphorus content of 0.5 phr.

The flame retardant may have been provided with a coating, which in the case of the compounding operation may also be applied subsequently. Suitable coatings are silanes such as vinylsilane or free fatty acids (or derivatives thereof) such as stearic acid, silicates, borates, aluminum compounds, phosphates, titanates, or else chelating agents. The amount of free fatty acid or derivative thereof is preferably between 0.3% and 1% by weight.

Particular preference is given to ground magnesium hydroxides, examples being brucite (magnesium hydroxide), kovdorskites (magnesium hydroxide phosphate), hydromagnesite (magnesium hydroxycarbon), and hydrotalcite (magnesium hydroxide with aluminum and carbonate in the crystal lattice), particular preference being given to the use of brucite. Admixtures of magnesium carbonates such as, for example, dolomite  $[\text{CaCO}_3 \cdot \text{MgCO}_3, M_r 184.41]$ , magnesite  $(\text{MgCO}_3)$ , and huntite  $[\text{CaCO}_3 \cdot 3\text{MgCO}_3, M_r 353.05]$  are allowable.

As far as aging is concerned, the presence of calcium carbonate (as the compound or in the form of a mixed crystal of calcium and magnesium and carbonate) in fact proves to be

advantageous, with a fraction of 1% to 4% by weight of calcium carbonate being regarded as favorable (the analytical calcium content is converted to pure calcium carbonate). In many deposits of brucite, calcium and carbonate are present as an impurity in the form of chalk, dolomite, huntite or hydrotalcite, but may also be mixed in deliberately to the magnesium hydroxide. The positive effect possibly derives from the neutralization of acids. These acids are formed, for example, from magnesium chloride, which is generally encountered as a catalyst residue in polyolefins (from the Spheripol process, for example). Acidic constituents from the adhesive coating may likewise migrate into the film and hence impair aging. By adding calcium stearate it is possible to obtain an effect similar to that achieved through calcium carbonate, but relatively large amounts reduce the bond strength of the adhesive coating in such winding tapes, and reduce in particular the adhesion of such an adhesive layer to the reverse face of the wrapping foil.

Particularly suitable magnesium hydroxide is that having an average particle size of more than 2  $\mu\text{m}$ , the reference being to the median value ( $d_{50}$  determined by laser light scattering by the Cilas method), and in particular of greater than or equal to 4  $\mu\text{m}$ . The specific surface area (BET) is preferably below 4  $\text{m}^2/\text{g}$  (DIN 66131/66132). Customary wet-precipitated magnesium hydroxides are finely divided; in general the average particle size is 1  $\mu\text{m}$  or below, the specific surface area 5  $\text{m}^2/\text{g}$  or more. The upper limit on the particle size distribution,  $d_{97}$ , is preferably not above 20  $\mu\text{m}$ , so as to prevent the occurrence of holes in the film and embrittlement. Therefore the magnesium hydroxide is preferably screened. The presence of particles with a diameter of 10 to 20  $\mu\text{m}$  gives the film a pleasing matt appearance.

The preferred particle morphology is irregularly spherical, similar to that of river pebbles. It is obtained preferably by grinding. Particular preference is given to magnesium hydroxide which has been produced by dry grinding in the presence of a free fatty acid, especially stearic acid. The fatty acid coating which forms enhances the mechanical properties of mixtures of magnesium hydroxide and polyolefins and reduces magnesium carbonate bloom. The use of a fatty acid salt (sodium stearate, for example) is likewise possible but has the drawback that the wrapping foil produced therefrom exhibits increased conductivity in the presence of moisture, which is deleterious for applications in which the wrapping foil also takes on the function of an insulating tape. In the case of synthetically precipitated magnesium hydroxide the fatty acid is always added in salt

form, owing to the water solubility. This is another reason why for the wrapping foil of the invention a ground magnesium hydroxide is preferred over a precipitated one.

Figures 1 to 3 depict various particle morphologies. Figure 1 shows regularly shaped, platelet-shaped particles; Figure 2 shows irregularly shaped, platelet-shaped particles; Figure 3 shows irregularly shaped, spherical particles.

Magnesium hydroxide in platelet form is less suitable. This is true of regular (for example, hexahedrons) and irregular platelets.

To the skilled worker the use of the finely divided synthetic magnesium hydroxide is obvious, since it is very pure and the flame retardancy is better than in the case of large particles. Surprisingly it has been found that compounds composed of ground magnesium hydroxide with relatively large spherical particles are processed more effectively in calendering and extrusion operations than compounds composed of ground magnesium hydroxide with small, platelet-shaped particles. Finely divided platelet-shaped magnesium hydroxide produces substantially higher melt viscosities than larger spherical magnesium hydroxide. The problem may be countered by polymers with a high melt index (MFI), but this impairs the mechanical stability of the melt, which is important particularly for blown-film extrusion and calendering. In the preferred embodiment the film is easier to remove from the rolls on the calender, or, respectively, the film bubble is more stable in the case of blown-film extrusion (the melt tube does not rupture), although the flame retardancy is somewhat poorer than in the case of synthetic magnesium hydroxide as preferred by the skilled worker. This can be countered by raising the filler content, although that presupposes a particularly soft polymer. This may be a soft ethylene homopolymer or ethylene copolymer, the film manufactured therefrom preferably being crosslinked in order to increase the thermal stability. The specific solution provided by the invention to this problem is a particularly soft polypropylene copolymer as set out above. This specific polymer makes it possible to a particular extent to use high amounts of filler, and even higher in the case of ground magnesium hydroxide, with a higher  $d_{50}$  value, without the wrapping foil becoming too rigid and inflexible for the application, and does not require any crosslinking. For applications under the influence of high service temperature the heavy metal traces in synthetic magnesium hydroxide may have an adverse effect on aging, which is prevented by the use of the specific aging inhibitor combinations specified below.

The amount of the flame retardant/retardants is chosen such that the wrapping foil is flame-retardant, i.e., slow burning. The flame spread rate according to FMVSS 302 with a horizontal sample is preferably below 200 mm/min, more preferably below 100 mm/min; in one outstanding embodiment of the wrapping foil it is self-extinguishing under these test conditions. The oxygen index (LOI) is preferably above 20%, in particular above 23%, and more preferably above 27%. When magnesium hydroxide (natural and synthetic) is used the fraction is preferably 70 to 200 phr and in particular 110 to 180 phr.

When 90 or more phr of filler is used the following techniques are preferred and claimed:

- Mixing of polymer and filler in a kneader in batch operation or continuously (from Banbury, for example); preferably, part of the filler is added when another part has already been homogenized with the polymer.
- Mixing of polymer and filler in a twin-screw extruder, part of the filler being used to prepare a pre-compound which in a second compounding step is mixed with the remainder of the filler.
- Mixing of polymer and filler in a twin-screw extruder, the filler being fed into the extruder not at one point but rather in at least two zones, through the use of a side feeder, for example.

Further additives customary in the case of films, such as fillers, pigments, aging inhibitors, nucleating agents, impact modifiers or lubricants, et cetera, can be used for the production of the wrapping foil. These additives are described for example in "Kunststoff Taschenbuch", Hanser Verlag, edited by H. Saechtling, 28th edition or "Plastic Additives Handbook", Hanser-Verlag, edited by H. Zweifel, 5th edition. In the remarks below the respective CAS Reg. No. is used in order to avoid chemical names that are difficult to understand.

The main objective of the present invention is high aging stability along with the absence of halogens and volatile plasticizers. As stated, the thermal requirements are going up, so that in addition an increased resistance is to be achieved with respect to conventional PVC wrapping foils or the PVC-free film winding tapes that are being trialed. The high aging stability is achieved by the use of an adequately metered and skillfully selected aging inhibitor combination (antioxidants and, if desired, metal deactivators) inclusively. The present invention is therefore described with reference to this in detail below.



The wrapping foil of the invention has a thermal stability of at least 105°C after 3000 hours, which means that after this storage there is still a breaking elongation of at least 100%. The foil ought further to have a breaking elongation of at least 100% after 20 days' storage at 136°C (accelerated test) and/or a heat resistance of 170°C (30 min). In one outstanding form with the antioxidants described and optionally also with a metal deactivator, 125°C after 2000 hours or even 125°C after 3000 hours are attained. Conventional PVC wrapping foils based on DOP have a heat stability of 85°C (passenger compartment), while high-performance products based on polymer plasticizer attain 105°C (engine compartment).

Furthermore, the wrapping foil must be compatible with polyolefin-based cable sheathing; in other words, after the cable/wrapping foil assembly has been stored, there must be neither embrittlement of the wrapping foil nor of the cable insulation. Through the selection of one or more appropriate antioxidants it is possible to attain a compatibility at 105°C, preferably at 125°C (2000 hours, in particular 3000 hours) and a short-term thermal stability of 140°C (168 hours).

A further prerequisite for adequate short-term thermal stability and heat resistance is a sufficient melting point on the part of the polyolefin (at least 120°C) and sufficient mechanical stability on the part of the melt somewhat above the crystallite melting point. The latter is ensured by a melt index of not more than 20 g/10 min for a filler content of at least 80 phr or of not more than 5 g/10 min for a filler content of at least 40 phr. It is, however, the aging stabilization which is decisive for attaining oxidative resistance above 140°C, and this is achieved in particular by means of secondary antioxidants such as phosphites.

Compatibility between wrapping foil and the other cable-harness components, such as plugs and fluted tubes, is likewise desirable and can likewise be achieved by adapting the formulas, particularly with respect to the additives. A negative example that may be recited is the combination of an unsuitable polypropylene wrapping foil with a copper-stabilized polyamide fluted tube; in this case both the fluted tube and the wrapping foil have undergone embrittlement after 3000 hours at 105°C.

The wrapping foil of the invention is preferably pigmented, especially black. Coloring may be carried out in the base film, in the adhesive layer or in any other layer. The use of organic pigments or dyes in the wrapping foil is possible, preference being given to the



use of carbon black. The carbon black fraction is preferably at least 5 phr, in particular at least 10 phr, since surprisingly it proves to have a significant influence on the fire performance. The thermal aging stability is, surprisingly, higher when the carbon black is added (in the form of a masterbatch, for example) only after the polypropylene polymer has been mixed with the aging inhibitors (antioxidants). This advantage can be utilized by first compounding polymer, aging inhibitor, and filler with one another and only adding the carbon black, as a masterbatch, in an extruder of the film production installation (calender or extruder). An additional benefit is that in the event of a product changeover on the compounder (plunger compounder or extruder such as twin-screw extruder or planetary roll extruder) there is no need for costly and inconvenient cleaning to remove carbon black residues. Surprisingly for the skilled worker, even unusually large amounts of carbon black masterbatch can be added without problems on the film installation, such amounts being not only 1 to 2 phr but even 15 to 30 phr. As carbon black it is possible to use all of the types, such as gas black, acetylene black, thermal black, furnace black and lamp black, for example, preference being given to lamp black, despite the fact that furnace blacks are usual for the coloring of films. For optimum aging, preference is given to carbon black grades having a pH in the range from 6 to 8, especially lamp black.

The wrapping foil is produced on a calender or by extrusion such as, for example, in a blowing or casting operation. These processes are described for example in Ullmann's Encyclopedia of Industrial Chemistry, 6th ed., Wiley-VCH 2002. The compound comprising the main components or all of the components can be produced in a compounder or kneading apparatus (for example, a plunger compounder) or extruder (for example, a twin-screw or planetary roll extruder) and then converted into a solid form (granules, for example) which are then melted in a film extrusion unit or in an extruder, compounder or roll mill of a calender installation, and processed further. High amounts of filler produce slight inhomogeneities (defects) which sharply reduce the breakdown voltage. The mixing operation must therefore be performed thoroughly enough that the foil manufactured from the compound attains a breakdown voltage of at least 3 kV/100  $\mu\text{m}$ , preferably at least 5 kV/100  $\mu\text{m}$ . It is preferred to produce compound and foil in one operation. The melt is supplied from the compounder directly to an extrusion unit or a calender, but may if desired pass through auxiliary installations such as filters, metal detectors or roll mills. In the course of the production operation the foil is oriented as little as possible, in order to achieve good hand tearability, low force value at 1% elongation, and low contraction. For this reason the calendering process is particularly preferred.

The contraction of the wrapping foil in machine direction after hot storage (30 minutes in an oven at 125°C, lying on a layer of talc) is less than 5%, preferably less than 3%.

5 The mechanical properties of the wrapping foil of the invention are situated preferably in the following ranges:

- breaking elongation in md (machine direction) from 300% to 1000%, more preferably from 500% to 800%,
- breaking strength in md in the range from 4 to 15, more preferably from 5 to 8 N/cm,

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the foil having been cut to size using sharp blades in order to determine the data.

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In the preferred embodiment the wrapping foil is provided on one or both sides, preferably one side, with a sealing or pressure-sensitive adhesive coating, in order to avoid the need for the wound end to be fixed by means of an adhesive tape, wire or knot. The amount of the adhesive layer is in each case 10 to 40 g/m<sup>2</sup>, preferably 18 to 28 g/m<sup>2</sup> (that is, the amount after removal of water or solvent, where necessary; the numerical values also correspond approximately to the thickness in µm). In one case with adhesive coating the figures given here for the thickness and for mechanical properties dependent on thickness refer exclusively to the polypropylene-containing layer of the wrapping foil, without taking into account the adhesive layer or other layers which are advantageous in connection with adhesive layers. The coating need not cover the whole area, but may also be configured for partial coverage. An example that may be mentioned is a wrapping foil with a pressure-sensitively adhesive strip at each of the side edges. This strip can be cut off to form approximately rectangular sheets, which are adhered to the cable bundle by one adhesive strip and are then wound until the other adhesive strip can be bonded to the reverse of the wrapping foil. A hoselike envelope of this kind, similar to a sleeve form of packaging, has the advantage that there is virtually no deterioration in the flexibility of the cable harness as a result of the wrapping.

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Suitable adhesives include all customary types, especially those based on rubber. Rubbers of this kind may be, for example, homopolymers or copolymers of isobutylene, of 1-butene, of vinyl acetate, of ethylene, of acrylic esters, of butadiene or of isoprene. Particularly suitable formulas are those based on polymers themselves based on acrylic esters, vinyl acetate or isoprene.

In order to optimize the properties it is possible for the self-adhesive mass employed to have been blended with one or more additives such as tackifiers (resins), plasticizers, fillers, flame retardants, pigments, UV absorbers, light stabilizers, aging inhibitors, photoinitiators, crosslinking agents or crosslinking promoters. Tackifiers are, for example, hydrocarbon resins (for example, polymers based on unsaturated C<sub>5</sub> or C<sub>9</sub> monomers), terpene-phenolic resins, polyterpene resins formed from raw materials such as  $\alpha$ - or  $\beta$ -pinene, for example, aromatic resins such as coumarone-indene resins, or resins based on styrene or  $\alpha$ -methylstyrene, such as rosin and its derivatives, disproportionated, dimerized or esterified resins, for example, such as reaction products with glycol, glycerol or pentaerythritol, for example, to name only a few, and also further resins (as recited, for example, in Ullmanns Enzyklopädie der technischen Chemie, Volume 12, pages 525 to 555 (4th ed.), Weinheim). Preference is given to resins without easily oxidizable double bonds, such as terpene-phenolic resins, aromatic resins, and, with particular preference, resins prepared by hydrogenation, such as, for example, hydrogenated aromatic resins, hydrogenated polycyclopentadiene resins, hydrogenated rosin derivatives or hydrogenated terpene resins.

Examples of suitable fillers and pigments include carbon black, titanium dioxide, calcium carbonate, zinc carbonate, zinc oxide, silicates or silica. Suitable admixable plasticizers are, for example, aliphatic, cycloaliphatic and aromatic mineral oils, diesters or polyesters of phthalic acid, trimellitic acid or adipic acid, liquid rubbers (for example, nitrile rubbers or polyisoprene rubbers of low molecular mass), liquid polymers of butene and/or isobutene, acrylic esters, polyvinyl ethers, liquid resins and soft resins based on the raw materials of tackifier resins, lanolin and other waxes or liquid silicones. Examples of crosslinking agents include isocyanates, phenolic resins or halogenated phenolic resins, melamine resins and formaldehyde resins. Suitable crosslinking promoters are, for example, maleimides, allyl esters such as triallyl cyanurate, and polyfunctional esters of acrylic and methacrylic acid. Examples of aging inhibitors include sterically hindered phenols, which are known, for example, under the trade name Irganox<sup>TM</sup>.

Crosslinking is advantageous, since the shear strength (expressed as holding power, for example) is increased and hence the tendency toward deformation in the rolls on storage (telescoping or formation of cavities, also called gaps) is reduced. Exudation of the pressure-sensitive adhesive mass, as well, is reduced. This is manifested in tack-free side edges of the rolls and tack-free edges in the case of the wrapping foil wound spirally around cables. The holding power is preferably more than 150 min.

The bond strength to steel ought to be situated in the range from 1.5 to 3 N/cm.

In summary the preferred embodiment has on one side a solvent-free self-adhesive mass  
 5 which has come about as a result of coextrusion, melt coating or dispersion coating. Dispersion adhesives are preferred, especially polyacrylate-based ones.

Advantageous is the use of a primer layer between wrapping foil and adhesive mass in  
 10 order to improve the adhesion of the adhesive mass on the wrapping foil and hence to prevent transfer of adhesive to the reverse of the foil during unwinding of the rolls.

Primers which can be used are the known dispersion- and solvent-based systems based  
 for example on isoprene or butadiene rubber and/or cyclo rubber. Isocyanate or epoxy  
 resin additives improve the adhesion and in part also increase the shear strength of the  
 15 pressure-sensitive adhesive. Physical surface treatments such as flaming, corona or plasma, or coextrusion layers, are likewise suitable for improving the adhesion. Particular preference is given to applying such methods to solvent-free adhesive layers, especially those based on acrylate.

The reverse face can be coated with known release agents (blended where appropriate  
 20 with other polymers). Examples are stearyl compounds (for example, polyvinyl stearylcarbamate, stearyl compounds of transition metals such as Cr or Zr, and ureas formed from polyethyleneimine and stearyl isocyanate), polysiloxanes (for example, as a copolymer with polyurethanes or as a graft copolymer on polyolefin), and thermoplastic  
 25 fluoropolymers. The term stearyl stands as a synonym for all linear or branched alkyls or alkenyls having a C number of at least 10, such as octadecyl, for example.

Descriptions of the customary adhesive masses and also reverse-face coatings and  
 primers are found for example in "Handbook of Pressure Sensitive Adhesive  
 30 Technology", D. Satas, (3rd edition). The stated reverse-face primer coatings and adhesive coatings are possible in one embodiment by means of coextrusion.

The configuration of the reverse face of the film may also, however, serve to increase the  
 adhesion of the adhesive mass to the reverse face of the wrapping foil (in order to control  
 35 the unwind force, for example). In the case of polar adhesives such as those based on acrylate polymers, for example, the adhesion of the reverse face to a film based on

polypropylene polymers is often not sufficient. For the purpose of increasing the unwind force an embodiment is claimed in which the polar reverse-face surfaces are achieved by corona treatment, flame pretreatment or coating/coextrusion with polar raw materials. Claimed alternatively is a wrapping foil in which the log product has been conditioned (stored under hot conditions) prior to slitting. Both processes may also be employed in combination. The wrapping foil of the invention preferably has an unwind force of 1.2 to 6.0 N/cm, very preferably of 1.6 to 4.0 N/cm, and in particular 1.8 to 2.5 N/cm, at an unwind speed of 300 mm/min. The conditioning is known in the case of PVC winding tapes, but for a different reason. In contradistinction to partially crystalline polypropylene copolymer films, plasticized PVC films have a broad softening range and, since the adhesive mass has a lower shear strength, owing to the migrative plasticizer, PVC winding tapes tend toward telescoping. This unadvantageous deformation of the rolls, in which the core is forced out of the rolls to the side, can be prevented if the material is stored for a relatively long time prior to slitting or is subjected briefly to conditioning (storage under hot conditions for a limited time). In the case of the process of the invention, however, the purpose of the conditioning is to increase the unwind force of material with an apolar polypropylene reverse face and with a polar adhesive mass, such as polyacrylate or EVA, since this adhesive mass exhibits extremely low reverse-face adhesion to polypropylene in comparison to PVC. An increase in the unwind force by conditioning or physical surface treatment is unnecessary with plasticized PVC winding tapes, since the adhesive masses normally used possess sufficiently high adhesion to the polar PVC surface.

In the case of polyolefin wrapping foils the significance of reverse-face adhesion is particularly pronounced, since because of the higher force at 1% elongation (owing to the flame retardant and the absence of conventional plasticizers) a much higher reverse-face adhesion, and unwind force, is necessary, in comparison to PVC film, in order to provide sufficient stretch during unwind for the application. The preferred embodiment of the wrapping foil is therefore produced by conditioning or physical surface treatment in order to achieve outstanding unwind force and stretch during unwind, the unwind force at 300 mm/min being higher preferably by at least 50% than without such a measure.

In the case of an adhesive coating, the wrapping foil is preferably stored beforehand for at least 3 days, more preferably at least 7 days, prior to coating, in order to achieve post-crystallization, so that the rolls do not acquire any tendency toward telescoping.



Preferably the foil on the coating installation is guided over heated rollers for the purpose of leveling (improving the planar lie), which is not customary for PVC wrapping foils.

Normally, polyethylene and polypropylene films cannot be torn into or torn off by hand. As partially crystalline materials, they can be stretched with ease and therefore have a high breaking elongation, generally of well above 500%.

When attempts are made to tear such films what occurs, rather than tearing, is stretching. Even high forces may not necessarily overcome the typically high rupture forces. Even if this does occur, the tear which is produced does not look good and cannot be used for bonding, since a thin, narrow "tail" is formed at either end. Nor can this problem be eliminated by means of additives, even if large amounts of fillers reduce the breaking elongation. If polyolefin films are biaxially stretched the breaking elongation is reduced by more than 50%, to the benefit of tearability. Attempts to transfer this process to soft wrapping foils fail, however, since there is a considerable increase in the 1% force value and the force/elongation curve becomes considerably steeper. A consequence of this is that the flexibility and conformability of the wrapping foil are drastically impaired. Moreover, it is found that films with such high filler content are virtually impossible to stretch in industrial production, owing to a high number of tears.

Surprisingly, a solution has been found by means of the slitting process when the rolls are being converted. In the course of the production of rolls of wrapping foils, rough slit edges are produced which, viewed microscopically, form cracks in the foil, which then evidently promote tear propagation. This is possible in particular through the use of a crush slitting with blunt rotating knives, or rotating knives with a defined sawtooth, on products in bale form (jumbo rolls, high-length rolls) or by means of a parting slitting with fixed blades or rotating knives on products in log form (rolls in production width and conventional selling length). The breaking elongation can be adjusted by appropriate grinding of the blades and knives. Preference is given to the production of log product with parting slitting using blunt fixed blades. By cooling the log rolls sharply prior to slitting it is possible to improve still further the formation of cracks during the slitting operation. In the preferred embodiment the breaking elongation of the specially slit wrapping foil is lower by at least 30% than when it is slit with sharp blades. In the case of the particularly preferred foils that are slit with sharp blades the breaking elongation is 500% to 800%; in the embodiment of the foil whose side edges are subjected to defined damage in the course of slitting, it is between 200% and 500%.



In order to increase the unwind force, the log product can be subjected to storage under hot conditions beforehand. Conventional winding tapes with cloth, web or film carriers (PVC for example) are slit by shearing (between two rotating knives), parting (fixed or rotating knives are pressed into a rotating log roll of the product), blades (the web is divided in the course of passage through sharp blades) or crushing (between a rotating knife and a roller).

The purpose of slitting is to produce saleable rolls from jumbo or log rolls, but not to produce rough slit edges for the purpose of easier hand tearability. In the case of PVC wrapping foils the parting slit is entirely conventional, since the process is economic in the case of soft foils. In the case of PVC material, however, hand tearability is given, since, unlike polypropylene, PVC is amorphous and therefore is not stretched on tearing, only elongated a little. So that the PVC films do not tear too easily, attention must be paid to appropriate gelling in the course of production of the film, which goes against an optimum production speed; in many cases, therefore, instead of standard PVC with a K value of 63 to 65, material of higher molecular weight is used, corresponding to K values of 70 or more. With the polypropylene wrapping foils of the invention, therefore, the reason for the parting is different than in the case of those made of PVC.

The wrapping foil of the invention is outstandingly suitable for the wrapping of elongate material such as ventilation pipes, field coils or cable looms in vehicles. The wrapping foil of the invention is likewise suitable for other applications, such as, for example, for ventilation pipes in air-conditioning installation, since the high flexibility ensures good conformability to rivets, beads and folds. Present-day occupational hygiene and environmental requirements are met, because halogenated raw materials are not used; the same also applies to volatile plasticizers, even though the amounts are so small that the fogging number is more than 90%. Absence of halogen is extremely important for the recovery of heat from wastes which include such winding tapes (for example, incineration of the plastics fraction from vehicle recycling). The product of the invention is halogen-free in the sense that the halogen content of the raw materials is so low that it plays no part in the flame retardancy. Halogens in trace amounts, such as may occur as a result of impurities, process additives (fluoroelastomers) or as residues of catalysts (from the polymerization of polymers, for example), remain disregarded. The omission of halogens is accompanied by the quality of easy flammability, which is not in accordance with the safety requirements in electrical applications such as household appliances or vehicles.

The problem of deficient flexibility when using customary PVC substitute materials such as polypropylene, polyethylene, polyesters, polystyrene, polyamide or polyimide for the wrapping foil is solved in the underlying invention not by means of volatile plasticizers but instead by the use of a polyolefin of low flexural modulus such as, for example, a soft PP copolymer. It is particularly surprising, therefore, that it is possible even to use fillers having a flame retardancy effect, which are known to impair the flexibility drastically to the point of complete embrittlement. The flexibility is of crucial importance, since application to wires and cables requires not only spiral winding but also creaseless curve-flexible winding at branching points, plugs or fastening clips. Moreover, it is desirable for the wrapping foil to draw the cable strand together elastically. This behavior is also needed for the sealing of ventilation pipes. These mechanical properties can be achieved only by a soft, flexible winding tape.

### Test Methods

The measurements are carried out under test conditions of  $23 \pm 1^\circ\text{C}$  and  $50 \pm 5\%$  relative humidity.

The density of the polymers is determined in accordance with ISO 1183 and the flexural modulus in accordance with ISO 178 and expressed in  $\text{g/cm}^3$  and MPa respectively. (The flexural modulus in accordance with ASTM D790 is based on different specimen dimensions, but the result is comparable as a number.) The melt index is tested in accordance with ISO 1133 and expressed in g/10 min. The test conditions are, as is the market standard,  $230^\circ\text{C}$  and 2.16 kg for polymers containing crystalline polypropylene and  $190^\circ\text{C}$  and 2.16 kg for polymers containing crystalline polyethylene. The crystallite melting point ( $T_{\text{cr}}$ ) is determined by DSC in accordance with MTM 15902 (Basell method) or ISO 3146.

The average particle size of the filler is determined by means of laser light scattering by the Cilas method, the critical figure being the  $d_{50}$  median value.

The specific surface area (BET) of the filler is determined in accordance with DIN 66131/66132.

The tensile elongation behavior of the wrapping foil is determined on type 2 test specimens (rectangular test strips 150 mm long and, as far as possible, 15 mm wide) in

accordance with DIN EN ISO 527-3/2/300 with a test speed of 300 mm/min, a clamped length of 100 mm and a pretensioning force of 0.3 N/cm. In the case of specimens with rough slit edges, the edges should be tidied up with a sharp blade prior to the tensile test. In deviation from this, for determining the force or tension at 1% elongation, measurement is carried out with a test speed of 10 mm/min and a pretensioning force of 0.5 N/cm on a model Z 010 tensile testing machine (manufacturer: Zwick). The testing machine is specified since the 1% value may be influenced somewhat by the evaluation program. Unless otherwise indicated, the tensile elongation behavior is tested in machine direction (MD). The force is expressed in N/strip width and the tension in N/strip cross section, the breaking elongation in %. The test results, particularly the breaking elongation (elongation at break), must be statistically ascertained by means of a sufficient number of measurements.

The bond strengths are determined at a peel angle of 180° in accordance with AFERA 4001 on test strips which (as far as possible) are 15 mm wide. AFERA standard steel plates are used as the test substrate, in the absence of any other substrate being specified.

The thickness of the wrapping foil is determined in accordance with DIN 53370. Any pressure-sensitive adhesive layer is subtracted from the total thickness measured.

The holding power is determined in accordance with PSTC 107 (10/2001), the weight being 20 N and the dimensions of the bond area being 20 mm in height and 13 mm in width.

The unwind force is measured at 300 mm/min in accordance with DIN EN 1944.

The hand tearability cannot be expressed in numbers, although breaking force, breaking elongation and impact strength under tension (all measured in machine direction) are of substantial influence.

#### Evaluation:

+++	=	very easy,
++	=	good,
+	=	still processable,
-	=	difficult to process,

- = can be torn only with high application of force; the ends are untidy,
- = unprocessable

The fire performance is measured in accordance with MVSS 302 with the sample horizontal. In the case of a pressure-sensitive adhesive coating on one side, that side faces up. As a further method, testing of the oxygen index (LOI) is performed. Testing for this purpose takes place under the conditions of JIS K 7201.

The thermal stability is determined by a method based on ISO/DIN 6722. The oven is operated in accordance with ASTM D 2436-1985 with 175 air changes per hour. The test time amounts to 3000 hours. Test temperatures chosen are 85°C (class A), 105°C (similar to class B but not 100°C), and 125°C (class C). Accelerated aging takes place at 136°C, with the test being passed if the elongation at break is still at least 100% after 20 days' aging.

In the case of compatibility testing, storage under hot conditions is carried out on commercially customary leads (cables) with polyolefin insulation (polypropylene or radiation-crosslinked polyethylene) for motor vehicles. For this purpose, specimens are produced from 5 leads with a cross section of 3 to 6 mm<sup>2</sup> and a length of 350 mm, with wrapping foil, by wrapping with a 50% overlap. After the aging of the specimens in a forced-air oven for 3000 hours (conditions as for thermal stability testing), the samples are conditioned at 23°C and in accordance with ISO/DIN 6722 are wound by hand around a mandrel; the winding mandrel has a diameter of 5 mm, the weight has a mass of 5 kg, and the winding rate is 1 rotation per second. The specimens are subsequently inspected for defects in the wrapping foil and in the wire insulation beneath the wrapping foil. The test is failed if cracks can be seen in the wire insulation, particularly if this is apparent even before bending on the winding mandrel. If the wrapping foil has cracks or has melted in the oven, the test is likewise classed as failed. In the case of the 125°C test, specimens were in some cases also tested at different times. The test time is 3000 hours unless expressly described otherwise in an individual case.

The short-term thermal stability is measured on cable bundles comprising 19 wires of type TW with a cross section of 0.5 mm<sup>2</sup>, as described in ISO 6722. For this purpose the wrapping foil is wound with a 50% overlap onto the cable bundle, and the cable bundle is bent around a mandrel with a diameter of 80 mm and stored in a forced-air oven at

140°C. After 168 hours the specimen is removed from the oven and examined for damage (cracks).

5 To determine the heat resistance the wrapping foil is stored at 170°C for 30 minutes, cooled to room temperature for 30 minutes and wound with at least 3 turns and a 50% overlap around a mandrel with a diameter of 10 mm. Thereafter the specimen is examined for damage (cracks).

10 In the case of the low-temperature test the above-described specimen is cooled to -40°C for 4 hours, in a method based on ISO/DIS 6722, and the sample is wound by hand onto a mandrel with a diameter of 5 mm. The specimens are visually examined for defects (cracks) in the adhesive tape.

15 The breakdown voltage is measured in accordance with ASTM D 1000. The number taken is the highest value for which the specimen withstands this voltage for one minute. This number is converted to a sample thickness of 100 µm.

Example:

20 A sample 200 µm thick withstands a maximum voltage of 6 kV for one minute: the calculated breakdown voltage amounts to 3 kV/100 µm.

The fogging number is determined in accordance with DIN 75201 A.

25 The examples which follow are intended to illustrate the invention without restricting its scope.

Contents:

- Tabular compilation of the raw materials used in the experiments
- Description of the inventive examples
- 30 ◦ Tabular compilation of the results of the inventive examples
- Description of the comparative examples
- Tabular compilation of the results of the comparative examples

35 Tabular compilation of the raw materials used for the experiments (the measurement conditions and units have in some cases been omitted; see Test Methods)

Raw material	Manufacturer	Description	Technical data
Polymer A		EP-modified random PP copolymer from reactor cascade, gas-phase process	Flexural modulus = 80 MPa, MFI = 0.6, Tcr = 142°C, Density = 0.88, Breaking stress 23 MPa, Yield stress 6 MPa
Polymer B		EP-modified random PP copolymer from reactor cascade, gas-phase process	Flexural modulus = 80 MPa, MFI = 8, Tcr = 142°C, Density = 0.88, Breaking stress 16 MPa, Yield stress 6 MPa
Polymer C		EP-modified random PP copolymer from reactor cascade, gas-phase process	Flexural modulus = 30 MPa, MFI = 0.6, Tcr = 141°C, Density = 0.87, Breaking stress 10 MPa
Polymer D		EP-modified random PP copolymer from a reactor, Sheripol process	Flexural modulus = 400 MPa, MFI = 0.8, Tcr = 140°C, Density = 0.9, Breaking stress 52 MPa
Cataloy KS-353 P	SKD Sunrise	EP-modified PP homopolymer, grafting in the Cataloy process	Flexural modulus = 83 MPa, MFI = 0.45, Tcr = 154°C, Density = 0.88, Breaking stress 10 MPa, Yield stress 6.2 MPa
Cataloy KS-021 P	SKD Sunrise	EP-modified PP homopolymer, grafting in the Cataloy process	Flexural modulus = 228 MPa, MFI = 0.9, Tcr = 154°C, Density = 0.89, Breaking stress 12 MPa, Yield stress 6.9 MPa



Lupolex 18E FA	Basell	LLDPE	Density = 0.919, MFI = 0.5
Affinity PL 1840	Dow Chem.	VLDPE	Density = 0.909, MFI = 1
Exact 8201	Exxon	LLDPE (metallocene)	Flexural modulus = 26 MPa, MFI = 1.1, T <sub>cr</sub> = 67°C, Density = 0.88, Breaking stress 20 MPa
Epsyn 7506	Copolymer	EPDM rubber	
Adflex KS 359 P	Basell	Ethylene-modified polypropylene homopolymer	Flexural modulus = 83 MPa, MFI = 12, T <sub>cr</sub> = 154°C, Density = 0.88, Breaking stress 10 MPa, Yield stress 5.0 MPa
ESI DE 200	Dow	Ethylene-styrene interpolymer	
Evaflex A 702	DuPont	EEA	EA = 19%, MFI = 5
Evaflex P 1905	DuPont	EVA	VAc = 19%, MFI = 5
Elvax 470	DuPont	EVA	VAc = 18%, MFI = 0.7
Evatane 2805	Elf Atochem	EVA	VAc = 28%, MFI = 5
Evatane 1005 VN4	Elf Atochem	EVA	VAc = 14%, MFI = 0.7
Escorene UL 00119	Exxon	EVA	VAc = 19%, MFI = 1
Escorene UL 02133	Exxon	EVA	VAc = 33, MFI = 21
Vinnapas B 100	Wacker	PVAc	VAc = 100%
Tuftec M-1943	Asahi Chemical	Diene-styrene elastomer	
Magnifin H 5	Martinswerk	Precipitated magnesium hydroxide	d <sub>50</sub> = 1.35 µm, platelet- shaped, BET = 4m <sup>2</sup> /g, >99.8% magnesium hydroxide, <0.1% calcium carbonate
Magnifin H 5 GV	Martinswerk	Precipitated magnesium hydroxide	d <sub>50</sub> = 1.35 µm, platelet- shaped BET = 4m <sup>2</sup> /g, >99.8% magnesium hydroxide, <0.1% calcium carbonate
Kisuma 5 A	Kisuma	Precipitated	d <sub>50</sub> = 1.0 µm, platelet-shaped

		magnesium hydroxide	
Brucite 15 $\mu$	Lehmann & Voss	Ground magnesium hydroxide	$d_{50} = 4 \mu\text{m}$ , $d_{97} = 18 \mu\text{m}$ , irregularly spherical, calcium carbonate content 2.4%, 0.5% stearic acid
Securoc B 10	Incemin	Ground magnesium hydroxide	$d_{50} = 4 \mu\text{m}$ , $d_{97} = 18 \mu\text{m}$ (screened), BET $8\text{m}^2/\text{g}$ , irregularly spherical, 0.3% fatty acid
Magshizu N-3 (Magseeds N-3)	Konoshima Chemical	Precipitated magnesium hydroxide	$d_{50} = 1.1 \mu\text{m}$ , platelet-shaped, BET = $3 \text{m}^2/\text{g}$ , 2.5% fatty acid coating
Martinal 99200-08 (Martinal OL 104 G)	Martinswerk	Aluminum hydroxide	$d_{50} = 1.8 \mu\text{m}$ , hexagonally platelet-shaped, BET = $4 \text{m}^2/\text{g}$ , polymer coating
Exolit AP 750	Clariant	Ammonium polyphosphate	
EDAP	Albright & Wilson	Ethylenediamine phosphate	
Flamestab NOR 116	Ciba-Geigy	Sterically hindered amine (HAS)	
SH 3	Dow Chemical	Calcium carbonate masterbatch	
DE 83 R	Great Lakes	Decabromodiphenyl oxide	
Antimony oxide TMS	Great Lakes	Diantimony trioxide	
Flammruß 101	Degussa	Lamp black	pH = 7.5
Carbon Black FEF	Shama Chemical	Furnace black	pH = 10
Seast 3 H	Tokai Carbon		pH = 9.5
Petrothene PM 92049	Equistar	Carbon black masterbatch comprising furnace	pH = 9, 40% furnace black in polyethylene

		black	
Novaexcel F-5	Rinkagaku/ Phosphorous Chemical	Red phosphorus	
A 0750	Union Carbide	Aminosilane	Crosslinker
AMEO T	Hüls AG	Aminosilane	Crosslinker
Irganox 1010	Ciba-Geigy	Primary antioxidant	Sterically hindered phenol
Irganox PS 800	Ciba-Geigy	Secondary antioxidant	Thiopropionic ester
Irganox PS 802	Ciba-Geigy	Secondary antioxidant	Thiopropionic ester
Sumilizer TPM	Sumitomo	Secondary antioxidant	Thiopropionic ester
Sumilizer TPL-R	Sumitomo	Secondary antioxidant	Thiopropiionic ester
Sumilizer TP-D	Sumitomo	Secondary antioxidant	Thiopropionic ester
Irgafos 168	Ciba-Geigy	Secondary antioxidant	Phosphite
Irganox MD 1024	Ciba-Geigy	Metal deactivator	Heavy-metal scavenger
Primal PS 83D	Rohm & Haas	Acrylate PSA	Dispersion PSA
Acronal DS 3458	BASF	Acrylate PSA	Hotmelt PSA
Rikidyne BDF 505	Vig te Qnos	Acrylate PSA	Solution PSA
JB 720	Johnson	Acrylate PSA	Dispersion PSA
Airflex EAF 60	Air Products	EVA PSA	Dispersion PSA
Desmodur Z 4470 MPA/X	Bayer	Isocyanate	Crosslinker

PSA = pressure-sensitive adhesive

### Example 1

- 5 To produce the carrier film, 100 phr of polymer A, 10 phr of Vinnapas B 10, 150 phr of Magnifin H 5 GV, 10 phr of Flammruß 101, 0.8 phr of Irganox 1010, 0.8 phr of Irganox PS

802 and 0.3 phr of Irgafos 168 are first compounded in a co-rotating twin-screw extruder. 1/3 of the Magnifin was added in each of zones 1, 3, and 5.

The compound melt is taken from the die of the extruder to a roll mill, from where it is passed through a strainer and subsequently fed via a conveyor belt into the nip of a calender of the "inverted L" type. With the aid of the calender rolls, a film having a smooth surface is formed in a width of 1500 mm and a thickness of 0.08 mm (80  $\mu$ m) and is post-crystallized on heat-setting rolls. The film is stored for one week, leveled on the coating installation with rolls at 60°C in order to improve the planar lie, and, following corona treatment, is coated with an aqueous acrylate PSA, Primal PS 83 D, by means of a coating knife, with an application rate of 24 g/m<sup>2</sup>. The layer of adhesive is dried in a drying tunnel at 70°C; the finished wrapping foil is wound to log rolls having a running length of 33 m on a 1-inch core (25 mm). Slitting takes place by parting the log rolls by means of a fixed blade with a not very acute angle (straight knife) into rolls 29 mm wide.

As in the case of the subsequent examples as well, in the parting slitting an automatic device is used, for the reasons set out in the description of the invention.

In spite of the high filler fraction, this self-adhesive wrapping foil exhibits good flexibility. Moreover, even without the addition of an oxygen-containing polymer, very good fire properties are achieved. The aging stability and the compatibility with PP and PA cables and polyamide fluted tube are outstanding.

### Example 2

The preparation takes place as in example 1, with the following changes: the compound is composed of 100 phr of polymer A, 120 phr of brucite 15  $\mu$ , 15 phr of Flammruß 101, 0.8 phr of Irganox 1010, 0.1 phr of Irganox PS 802, 0.1 phr of Sumilizer TPN, 0.1 phr of Sumilizer TPL-R, 0.1 phr of Sumilizer TP-D, 0.3 phr of Irgafos 168 and 1 phr of Irganox MD 1024. 1/2 of the brucite was added in each of zones 1 and 5.

The carrier film produced from this compound is subjected to flame pretreatment on one side and, after 10 days' storage, is coated with Acronal DS 3458 by means of a roll applicator at 50 m/min. The temperature load on the carrier is reduced by means of a cooled counterpressure roller. The application rate is about 35 g/m<sup>2</sup>. Appropriate crosslinking is achieved in-line, before winding, by irradiation with a UV unit equipped with 6 medium-pressure Hg lamps each of 120 W/cm. The irradiated web is wound to form log

rolls with a running length of 33 m on a 1 1/4-inch core (31 mm). For the purpose of increasing the unwind force, the log rolls are conditioned in an oven at 60°C for 5 hours. Slitting takes place by parting of the log rolls by means of a fixed blade (straight knife) into rolls 25 mm wide.

5

After three months' storage at 23°C no aging inhibitor has exuded from the foil. Foil from example 1, in comparison, has a light coating, which analysis shows to be composed of Irganox PS 802.

10

This wrapping foil is distinguished by even greater flexibility than that from example 1. The flame spread rate is more than sufficient for the application. The foil has a slightly matt surface. With respect to application, two fingers can be accommodated in the core, which facilitates application as compared with example 1.

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### Example 3

Production takes place as in example 1, with the following changes:

20

the compound is composed of 80 phr of polymer A, 20 phr of Evaflex A 702, 120 phr of Securoc B 10, 0.2 phr of calcium carbonate, 10 phr of Flammruß 101, 0.8 phr of Irganox 1010, 0.8 phr of Irganox PS 802 and 0.3 phr of Irgafos 168.

25

The film is corona-treated upstream of the calender winding station and on this side of the adhesive mass Rikidyne BDF 505 is applied (with the addition of 1% by weight of Desmodur Z 4470 MPA/X per 100 parts by weight of adhesive mass, calculated on the basis of solids content) at 23 g/m<sup>2</sup>. The adhesive is dried in a heating tunnel, in the course of which it is chemically crosslinked, and at the end of the dryer it is wound up into jumbo rolls, gently corona-treated on the uncoated side after 1 week, and at that stage

30

rewound to give log rolls with a running length of 25 m. These log rolls are stored in an oven at 100°C for 1 hour. The log rolls are slit by parting by means of a slightly blunt, rotating blade (round blade) into rolls with a width of 15 mm.

35

This wrapping foil features balanced properties and has a slightly matt surface. The holding power is more than 2000 min (at which point measurement was terminated). The



breaking elongation is 36% lower than in the case of samples with blade slitting. The unwind force is 25% higher than in the case of samples without conditioning.

#### Example 4

5

Production takes place as in example 1, with the following changes:

the compound is composed of 100 phr of polymer A, 120 phr of Magnifin H 5 GV, 10 phr of Flammruß 101, 2 phr of Irganox 1010, 1.0 phr of Irganox PS 802 and 0.4 phr of Irgafos 168.

10

After one week's storage, the film is flame-pretreated on one side and coated at 30 g/m<sup>2</sup> (dry application) with Airflex EAF 60. The web is dried initially with an IR lamp and then to completion in a tunnel at 100°C. Subsequently the tape is wound up to form jumbo rolls (large rolls). In a further operation the jumbo rolls are unwound and the uncoated side of

15

the wrapping foil is subjected to weak corona treatment in a slitting machine for the purpose of increasing the unwind force, and is processed by blunt crush cutting to give rolls 33 m long in a width of 19 mm on a 1 1/2-inch core (37 mm inside diameter). The breaking elongation is 48% lower than in the case of samples with blade cutting. The unwind force is 60% higher than in the case of samples without corona treatment. With

20

respect to application, two fingers can be accommodated in the core, which facilitates winding in relation to example 1.

#### Example 5

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The compound is produced on a pin extruder (Buss) without carbon black, with underwater granulation. After drying, the compound is mixed with the carbon black masterbatch in a concrete mixer.

30

The carrier film is produced on a blown-film extrusion line, using the following formula: 100 phr of polymer B, 100 phr of brucite 15 µ, 20 phr of a masterbatch of 50% Flammruß 101 and 50% polyethylene, 0.8 phr of Irganox 1076, 0.8 phr of Irganox PS 800, 0.2 phr of Ultrinox 626 and 0.6 phr of Naugard XL-1.

35

The film bubble is slit and opened with a triangle to give a flat web, which is guided via a heat-setting station, corona treated on one side and stored for a week for post-crystallization. For leveling (improvement of the planar lie) the film is guided over

5 preheating rolls on the coating line, coating otherwise taking place with pressure-sensitive adhesive in the same way as in example 1, and then the log rolls are conditioned at 65°C for 5 hours and slit as in example 1.

- 5 Without heat-setting, the film exhibits marked contraction (5% in width, length not measured) during the drying operation. The planar lie of the freshly produced film is good, and it is coated immediately after extrusion; unfortunately, after three weeks' storage at 23°C, the rolls have already undergone marked telescoping.  
This problem can also not be eliminated by conditioning the log rolls (10 hours at 70°C).
- 10 Thereafter the film is stored for a week prior to coating; telescoping of the rolls is now only partial, but in the course of coating the planar lie is so poor and the application of adhesive so irregular that preheating rolls were installed on the line.
- 15 The film features good heat resistance, i.e. without melting or embrittlement, in the case of additional storage at 170°C for 30 minutes.

### Example 6

- 20 Production takes place as in example 1, with the following changes:  
the film contains 80 phr of polymer C, 20 phr of Escorene UL 00119, 130 phr of Kisuma 5 A, 15 phr of Flammruß 101, 0.8 phr of Irganox 1010, 0.8 phr of Irganox PS 802 and 0.3 phr of Irgafos 168.
- 25 This carrier film is corona treated on one side and stored for a week. The pretreated side is coated with 0.6 g/m<sup>2</sup> of an adhesion promoter layer comprising natural rubber, cyclo rubber and 4,4'-diisocyanatodiphenylmethane (solvent: toluene) and dried. The coating of adhesive mass is applied directly to the adhesion promoter layer using a comma bar with an application weight of 18 g/m<sup>2</sup> (based on solids). The adhesive mass is composed of a
- 30 solution of a natural rubber adhesive mass in n-hexane with a solids content of 30 percent by weight. These solids are made up of 50 parts of natural rubber, 10 parts of zinc oxide, 3 parts of rosin, 6 parts of alkylphenolic resin, 17 parts of terpene-phenolic resin, 12 parts of poly-β-pinene resin, 1 part of Irganox 1076 antioxidant and 2 parts of mineral oil. The subsequent coat is dried in a drying tunnel at 100°C. Immediately
- 35 downstream of this, the film is slit in a composite automatic slitter featuring a knife bar

with sharp blades at a distance of 19 mm, to form rolls on standard adhesive-tape cores (3 inch).

Despite its high filler fraction, this wrapping foil is distinguished by very high flexibility, which is reflected in a low force value at 1% elongation. This wrapping foil has mechanical properties similar to those of plasticized PVC winding tapes, and is even superior in terms of flame retardancy and thermal stability. The holding power is 1500 min and the unwind force at 30 m/min (not 300 mm/min) is 5.0 N/cm. The fogging number is 62% (probably as a result of the mineral oil in the adhesive). Because of the large diameter of the roll, the roll can be pulled through only obliquely between winding board and cable harness, producing creases in the winding.

### Example 7

The compounds for the individual layers of the film are produced without carbon black in a compounder with extruder and underwater granulation. The mixing time before homogenization is 2 minutes, while the total kneading time before discharge into the granulating extruder is 4 minutes. In the case of the compound for layers 2 and 3, half of the filler is added at the beginning and the other half after 1 minute. After drying, the granules of compound are mixed with the carbon black masterbatch in a concrete mixer and the mixture is supplied to a 3-layer coextrusion line in accordance with the casting process (die width 1400 mm, die-head melt temperature 190°C, chill-roll temperature 30°C, speed 30 m/min).

The make-up of the formula of the carrier film is as follows:

Layer 1:

15 µm: 100 phr of Evaflex P 1905, 40 phr of Magnifin H 5 GV, 20 phr of a masterbatch of 50% Flammruß 101 and 50% polyethylene, 0.4 phr of Irganox 1076 and 0.2 phr of Irgafos 168

Layer 2:

40 µm: 100 phr of polymer B, 120 phr of Magnifin H 5 GV, 20 phr of a masterbatch of 50% Flammruß 101 and 50% polyethylene, 0.8 phr of Irganox 1076, 0.8 phr of Irganox PS 800 and 0.2 phr of Irgafos 168

Layer 3:

40  $\mu\text{m}$ : as layer 2

Layer 4:

5 15  $\mu\text{m}$ : 100 phr of Escorene UL 02133, 0.4 phr of Irganox 1076 and 0.2 phr of Irgafos 168

Layer 5:

20  $\mu\text{m}$ : Levapren 450

10 Because of problems that occurred with the blown film, the film is heat-set.  
After a week of storage at 23°C the film is coated as in example 1, but using the leveling rolls. The wrapping foil thus obtained is wound into log rolls with a running length of 20 m, which are conditioned at 40°C for one week. Slitting takes place by parting of the log rolls using a fixed blade (straight knife).

15

In a preliminary experiment a mixing time of 2 minutes was chosen; the film is homogeneous (no specks of filler) but the breakdown voltage is only 3 kV/100  $\mu\text{m}$ . Therefore, in spite of the risk of degradation, the mixing time is increased (the melt index, as a measure of degradation, undergoes only an immaterial increase as a result of the longer time, owing to the use of phosphite stabilizer). This material has no bond strength for steel and adheres poorly to the reverse. This adhesion is enough to ensure that the turns do not shift relative to one another, but at the end of winding it is necessary to carry out final fastening with a pressure-sensitively adhesive wrapping foil.

20

As a result of the conditioning, the unwind force rises to such a degree that the wrapping foil can be applied under slight tension. This embodiment is solvent-free and easy to produce, since no coating is required.

25

As a result of the colored layer 1, which comprises little flame retardant, the wrapping foil exhibits virtually no stress whitening under high elongation. The fogging number is 97%.

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For application, two fingers can be accommodated in the core, which makes winding easier than in example 1, without the problem described in example 6 occurring.

Relative to the other inventive examples and to the comparative examples based on polyolefin and magnesium hydroxide, the foil has the feature that, on elongation of more than 20%, no stress whitening is in evidence, since the outermost layer has only a low filler fraction, which is also attached effectively to the polar polymer. As a result of the

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presence of polar polymer, the fire performance is nevertheless excellent and the polypropylene-containing layers prevent melting of the foil.

### Example 8

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Production takes place in the same way as in example 1, with the following changes:

the compound consists of 30 phr of polymer D, 70 phr of Exact 8201, 50 phr of Exolit AP 750, 0.3 phr of Flamestab NOR 116, 10 phr of a masterbatch of 50% Flammruß and 50% polyethylene, and 4.5 phr of Irganox 1010. Further operation takes place as in example 1, with slitting taking place as in example 6.

10

This film is distinguished by improved hand tearability.



**Properties of the inventive examples**

	<b>Example</b>	<b>Example</b>	<b>Example</b>	<b>Example</b>	<b>Example</b>	<b>Example</b>	<b>Example</b>	<b>Example</b>	<b>Example</b>
	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	
Film thickness [mm]	0.08	0.09	0.095	0.085	0.06	0.11	0.13	0.08	
Bond strength steel [N/cm]	2.9	3.0	2.4	1.9	2.8	3.0	1.9	2.9	
Bond strength to own reverse [N/cm]	1.9	2.2	1.8	1.6	1.7	1.8	1.7	1.8	
Unwind force [N/cm]	2.2	2.4	2.0	1.8	2.5	2.7	2.0	2.0	
Tensile strength* [N/cm]	10.2	7.2	11.1	6.8	4.1	9.0	7.5	7.5	
Breaking elongation* [%]	760	980	860	830	600	1044	770	750	
Force at 1% elongation [N/cm]	2.1	2.8	2.1	2.0	1.4	1.7	2.0	1.3	
Force at 100% elongation [N/cm]	5.7	8.5	9.7	5.1	3.2	5.3	5.5	4.3	
Breaking elongation* after 20 d @ 136°C[%]	380	570	410	620	350	530	520	150	
Breaking elongation* after 3000 h @ 105°C >100%	yes	yes	yes	yes	yes	yes	yes	yes	
Thermal stability 168 h @ 140°C	yes	yes	yes	yes	yes	yes	yes	yes	
Heat resistance 30 min @ 170°C	yes	yes	yes	yes	yes	yes	yes	yes	
Compatibility with PE and PP cables 3000 h @ 105°C	no embrittle- ment	no embrittle- ment	no embrittle- ment	no embrittle- ment	no embrittle- ment	no embrittle- ment	no embrittle- ment	no embrittle- ment	
Compatibility with PE and PP cables 2000 h @ 125°C	no embrittle-	no embrittle-	no embrittle-	no embrittle-	no wrapping foil	no embrittle-	no embrittle-	no embrittle-	

**SUBSTITUTE SPECIFICATION**

	Example	Example	Example	Example	Example	Example	Example	Example
	1	2	3	4	5	6	7	8
	ment	ment	ment	ment	brittle	ment	ment	ment
Hand tearability	++	++	+	++	+++	--	++	+++
LOI [%]	22.6	20.3	22.0	20.1	20.0	24.1	20.5	25.8
Flame spread rate	45	170	63	160	183	self-extinguishing	197	self-extinguishing
FMVSS 302 [mm/min]								
Breakdown voltage [kV/100 µm]	6	5	6	5	7	6	5	4
Fogging number	95	92	94	99	93	62	97	95
Absence of halogen	yes	yes	yes	yes	yes	yes	yes	yes
Phosphorus content >0.5 phr	yes	yes	yes	yes	yes	yes	yes	yes

\* on specimens slit using blades

### Comparative example 1

Coating is carried out using a conventional film for insulating tape, from Singapore Plastic Products Pte, under the name F2104S. According to the manufacturer the film contains  
5 about 100 phr (parts per hundred resin) of suspension PVC with a K value of 63 to 65,  
43 phr of DOP (di-2-ethylhexyl phthalate), 5 phr of tribasic lead sulfate (TLB, stabilizer),  
25 phr of ground chalk (Bukit Batu Murah Malaysia with fatty acid coating), 1 phr of  
furnace black and 0.3 phr of stearic acid (lubricant). The nominal thickness is 100  $\mu\text{m}$  and  
the surface is smooth but matt.

10

Applied to one side is the primer Y01 from Four Pillars Enterprise, Taiwan (analytically  
acrylate-modified SBR rubber in toluene) and atop that 23  $\text{g/m}^2$  of the adhesive IV9 from  
Four Pillars Enterprise, Taiwan (analytically determinable main component: SBR and  
natural rubber, terpene resin and alkylphenolic resin in toluene). Immediately downstream  
15 of the dryer, the film is slit to rolls in an automatic composite slitter having a knife bar with  
sharp blades at a distance of 25 mm.

15

The elongation at break after 3000 h at 105°C cannot be measured, since as a result of  
plasticizer evaporation the specimen has disintegrated into small pieces. After 3000 h at  
20 85°C the breaking elongation is 150%.

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### Comparative example 2

Example 4 of EP 1 097 976 A1 is reworked.

25

The following raw materials are compounded in a compounder: 80 phr of  
Cataloy KS-021 P, 20 phr of Evaflex P 1905, 100 phr of Magshizu N-3, 8 phr of  
Norvaexcel F-5 and 2 phr of Seast 3H, and the compound is granulated, but the mixing  
time is 2 minutes.

30

In a preliminary experiment it is found that with a mixing time of 4 minutes the melt index  
of the compound increases by 30% (which may be due to the absence of a phosphite  
stabilizer or to the greater mechanical degradation owing to the extremely low melt index  
of the polypropylene polymer). Although the filler was dried beforehand and a venting  
35 apparatus is located above the kneading compounder, a pungent phosphine odor is  
formed on the line during kneading.

35

The carrier film is subsequently produced by means of extrusion as described in example 7 (with all three extruders being fed with the same compound) via a slot die and chill roll in a thickness of 0.20 mm, the rotational speed of the extruder being reduced until the film reaches a speed of 2 m/min.

In a preliminary experiment it is not possible to achieve the speed of 30 m/min as in example 7, since the line shuts down owing to excess pressure (excessive viscosity).

In a further preliminary experiment the film is manufactured at 10 m/min; the mechanical data in machine and cross directions pointed to a strong lengthwise orientation, which is confirmed in the course of coating by a 20% contraction in machine direction.

The experiment is therefore repeated with an even lower speed, which gives a technically flawless (including absence of specks) but economically untenable film.

Coating takes place in the same way as in example 3, but with adhesive applied at 30 g/m<sup>2</sup> (the composition of this adhesive is similar to that of the original adhesive of the patent example reworked). Immediately downstream of the dryer, the film is divided into strips 25 mm wide, using a knife bar with sharp blades, and in the same operation is wound into rolls.

The self-adhesive winding tape is notable for a lack of flexibility. As compared with example 5 or 6, the rigidity of comparative example 2 is higher by 4030% or 19 000%, respectively.

As is known, the rigidity can be calculated easily from the thickness and the force at 1% elongation (proportional to the elasticity modulus). Because of the red phosphorus it contains, and because of the relatively high thickness, the specimen exhibits very good fire performance (note: the LOI value is measured on the 0.2 mm thick sample with adhesive, whereas the LOI of 30% in the cited patent originates from a 3 mm thick test specimen without adhesive).

### **Comparative example 3**

Example A of WO 97/05206 A1 is reworked.

The production of the compound is not described. The components are therefore mixed on a twin-screw laboratory extruder with a length of 50 cm and an L/D ratio of 1:10: 9.59 phr of Evatane 2805, 8.3 phr of Attane SL 4100, 82.28 phr of Evatane 1005 VN4,

74.3 phr of Martinal 99200-08, 1.27 phr of Irganox 1010, 0.71 phr of AMEO T, 3.75 phr of black masterbatch (prepared from 60% by weight of polyethylene with MFI = 50 and 40% by weight of Furnace Seast 3 H), 0.6 phr of stearic acid and 0.60 phr of Luwax AL 3.

- 5 The compound is granulated, dried and blown on a laboratory line to form a film bubble, which is slit both sides. An attempt is made to coat the film with adhesive after corona pretreatment, as in example 1; however, the film exhibits excessive contraction in the cross and machine directions, and because of excessive unwind force it is hardly still possible to unwind the rolls after 4 weeks.

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This is therefore followed by an experiment at coating with an apolar rubber adhesive as in example 6, but this attempt fails because of the sensitivity of the film to solvent. Since the publication indicated does not describe coating with adhesive, but does describe adhesive properties that are to be aimed at, the film is slit up with shears between a set of  
15 pairs of two rotating knives each, to give strips 25 mm wide, which are wound.

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The self-adhesive winding tape features good flexibility and flame retardancy. The hand tearability, however, is inadequate. A particular disadvantage, though, is the low heat distortion resistance, which leads to the adhesive tape melting when the aging tests are carried out. Moreover, the winding tape results in a considerable shortening of the lifetime of the cable insulation, as a result of embrittlement. The high contraction tendency is caused by the inadequate melt index of the compound. Even with a higher melt index of the raw materials, problems are likely, despite the fact that the contraction will become much lower as a result, since no heat-setting is envisaged in the stated publication,  
25 despite the low softening point of the film. Since the product exhibits no significant unwind force it is almost impossible to apply to wire bundles. The fogging number is 73% (probably owing to the paraffin wax).

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#### Comparative example 4

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Example 1 of EP 0 953 599 A1 is reworked.

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The preparation of the compound is mixed as described on a single-screw laboratory extruder: 85 phr of Lupolex 18 E FA, 6 phr of Escorene UL 00112, 9 phr of Tuftec M-1943, 63 phr of Magnifin H 5, 1.5 phr of magnesium stearate, 11 phr of



Novaexcel F 5, 4 phr of Carbon Black FEF, 0.2 phr of Irganox 1010 and 0.2 phr of Tinuvin 622 LD, a marked release of phosphine being apparent from its odor.

Film production takes place as in comparative example 3.

5

The film, however, has a large number of specks of filler and has small holes, and the bubble tears a number of times during the experiment. The breakdown voltage varies widely from 0 to 3 kV/100  $\mu$ . For further homogenization, therefore, the granules are melted again in the extruder and granulated. The compound now obtained has only a small number of specks. Coating and slitting take place as in example 1.

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Through the use of red phosphorus, the self-adhesive winding tape features very good flame retardancy. Since the product has no unwind force, it is virtually impossible to apply to wire bundles. The thermal stability is inadequate, owing to the low melting point.

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#### **Comparative example 5**

A UV-crosslinkable acrylate hotmelt adhesive of the type Acronal DS 3458 is applied by means of nozzle coating at 50 m/min to a textile carrier of the Maliwatt stitchbonded knit filament web type (80 g/m<sup>2</sup>, 22 denier, black, thickness about 0.3 mm). The temperature load on the carrier is reduced by means of a cooled counterpressure roll. The application rate is about 65 g/m<sup>2</sup>. Appropriate crosslinking is achieved in-line, upstream of the winding process, by irradiation with a UV unit equipped with 6 medium-pressure Hg lamps each of 120 W/cm. The bales are converted by shearing slitting (between a set of rotating blades slightly offset in pairs) to give rolls on standard 3-inch cores.

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This winding tape features good adhesive properties and also very good compatibility with different cable insulation materials (PVC, PE, PP) and fluted tubes. From a performance standpoint, however, the high thickness and the absence of hand tearability are very disadvantageous.

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#### **Comparative example 6**

Example 1 of US 5,498,476 A1 is reworked.

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The following mixture is prepared in a Brabender plastograph (mixing time 5 min): 80 phr of Elvax 470, 20 phr of Epsyn 7506, 50 phr of EDAP, 0.15 phr of A 0750 and 0.15 phr of Irganox 1010.

- 5 The compound is compressed in a heated press between two sheets of siliconized polyester film to give test specimens 0.2 mm thick, which are cut into strips 25 mm wide and 25 cm long and wound onto a core to form a small roll. Coating with adhesive does not take place according to the specification.
- 10 This wrapping foil possesses neither acceptable flexibility nor resistance to melting. Since the product has no unwind force, it is virtually impossible to apply to wire bundles. It is difficult to tear into by hand. The breakdown voltage is relatively high, since the mixture is evidently very homogeneous, the Brabender mixer carries out mixing very intensely, and the aminosilane might also make a positive contribution, as suggested by the
- 15 force/elongation curves of the cited patent.

#### **Comparative example 7**

Example 1 of WO 00/71634 A1 is reworked.

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The following mixture is produced in a compounder: 80.8 phr of ESI DE 200, 19.2 phr of Adflex KS 359 P, 30.4 phr of calcium carbonate masterbatch SH3, 4.9 phr of Petrothen PM 92049, 8.8 phr of antimony oxide TMS and 17.6 phr of DE 83-R.

- 25 The compound is processed to flat film on a laboratory casting line, corona pretreated, coated at 20 g/m<sup>2</sup> with JB 720, wound into log rolls with a 3-inch core, and slit by parting with a fixed blade (advanced by hand).

- 30 This winding tape features PVC-like mechanical behavior: that is, high flexibility and good hand tearability. A disadvantage is the use of brominated flame retardants. Moreover, the heat distortion resistance at temperatures above 95°C is low, so that the film melts during the aging and compatibility tests.

### Properties of the comparative examples

	Comp. ex. 1	Comp. ex. 2	Comp. ex. 3	Comp. ex. 4	Comp. ex. 5	Comp. ex. 6	Comp. ex. 7
Film thickness [mm]	0.08	0.20	0.15	0.20	0.29	0.20	0.125
Bond strength steel [N/cm]	1.8	3.3	2.0	1.9	5.1	2.2	2.3
Bond strength to own reverse [N/cm]	1.6	1.5	1.8	1.4	1.5	1.6	1.2
Unwind force [N/cm]	2.0	1.8	1.9	1.7	3.5	2.1	1.5
Tensile strength* [N/cm]	15	10.9	22.3	44.0	51.3	16.1	22.5
Breaking elongation* [%]	150	370	92	720	72	720	550
Force at 1% elongation [N/cm]	1.0	11.4	4.3	5.9	5.2	3.5	0.46
Force at 100% elongation [N/cm]	14.0	9.2	--	19.8	--	9.1	6.3
Breaking elongation* after 20 d @ 136°C [%]	embrittled	embrittled	melted	Melted	60	melted	melted
Breaking elongation* after 3000 h @ 105°C >100%	embrittled	embrittled	yes	yes	not embrittled	embrittled	embrittled
Compatibility with PE and PP cables 3000 h @ 105°C	no	PE yes PP no	cable embrittled	tape fragile	yes	no	tape fragile
Thermal stability 168 h @ 140°C	no	yes	no	no	yes	no	no
Heat stability 30 min @ 170°C	no	yes	no	no	yes	no	no
Compatibility with PE and PP cables 2000 h @ 125°C	no	no	tape melted	tape melted	yes	no	tape melted
Hand tearability	+++	--	-	--	--	+	+

	Comp. ex. 1	Comp. ex. 2	Comp. ex.	Comp. ex. 4	Comp. ex.	Comp. ex.	Comp. ex. 7
LOI [%]	21.4	27.1	3	28.3	5	6	32.6
Flame spread rate according to FMVSS 302 [mm/min]	324	self-extinguishing	463	self-extinguishing	362	213	self-extinguishing
Breakdown voltage [kV/100 µm]	4	2	3	3	4	4	4
Fogging number	29	66	73	63	99	53	73
Absence of halogen	no	yes	yes	yes	yes	yes	no
Phosphorus content <0.5 phr	yes	no	yes	no	yes	no	yes

\* on specimens slit using blades